

Weak non-linear surface charging effects in electrolytic films

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(Dated: 7 October 2002)

A simple model of soap films with nonionic surfactants stabilized by added electrolyte is studied. The model exhibits charge regularization due to the incorporation of a physical mechanism responsible for the formation of a surface charge. We use a Gaussian field theory in the film but the full non-linear surface terms which are then treated at a one-loop level by calculating the mean-field Poisson-Boltzmann solution and then the fluctuations about this solution. We carefully analyze the renormalization of the theory and apply it to a triple layer model for a thin film with Stern layer of thickness h . For this model we give expressions for the surface charge $\sigma(L)$ and the disjoining pressure $P_d(L)$ and show their dependence on the parameters. The influence of image charges naturally arise in the formalism and we show that predictions depend strongly on h because of their effects. In particular, we show that the surface charge vanishes as the film thickness $L \rightarrow 0$. The fluctuation terms about this class of theories exhibit a Casimir-like attraction across the film and although this attraction is well known to be negligible compared with the mean-field component for thick films in the presence of electrolyte, in the model studied here these fluctuations also affect the surface charge regulation leading to a fluctuation component in the disjoining pressure which has the same behavior as the mean-field component even for large film thickness.

I. INTRODUCTION

Many situations in colloid, polymer and inter-facial science involve charged objects interacting in electrolyte solutions. In the case of two interacting membranes or soap films one encounters the electric double-layer. The mean-field theory of such experimental configurations is the Poisson-Boltzmann theory [1, 2] for which a surface boundary condition must be determined. For example, the surface charge or surface potential can be given, or a relation between the surface charge and surface potential may be specified. Such a relationship arises in a charge regularized model where the surface charging mechanism is derived from a microscopic description of the chemistry and geometry at the interface. Charge regularized models have the property that, owing to the thermodynamic nature of the charging mechanism, the surface charge changes as the distance between the two surfaces varies. The variation of the surface charge with the inter-surface distance will also change the effective interaction between the surfaces and consequently also the disjoining pressure. Within the film, the mean-field Poisson-Boltzmann theory is only sensitive to the electrostatic properties of the electrolyte; the chemistry and effective sizes of the ions in the system only enter into the description of the surface charging process. For example experiments [3] shows that the disjoining pressure increases with increasing hydration radius of the counter-ions in ionic soap films. This effect can be explained by the fact that as the counter ion radius increases the capacity for it to approach the surface and screen the surface charge is reduced.

To take into account bulk surface tensions of electrolytes one must resort to a microscopic description of the physics at the interfaces. Depending on the nature of interface one may have specific adsorption due to chemical effects which can be taken into account via the law of mass action [4, 5, 6, 7, 8] or at a more statistical mechanical level by introducing an external potential at the surface which models the chemical liaison involved [9, 10, 11]. In addition, there are other forces which come into play which are not present in the standard Poisson-Boltzmann approach. These are effects due to fluctuations in the electromagnetic field which can be identified with van der Waals forces [12, 13, 14]. In bulk, the non-zero frequency van der Waals forces have little effect on the static ionic distributions since the relevant frequencies are too large and their contributions can be decoupled from those of zero frequency. However, it was pointed out in [15] that near interfaces the non-zero frequency van der Waals or dispersion forces can be important and depend strongly on the polarizability of the ions involved and hence are ion specific. The zero frequency van der Waals forces, which correspond to thermal fluctuations in the electrostatic field, do strongly influence ionic distributions and so do modify the surface charge.

When there are spatial variations in the dielectric constant image charges arise [16]. In the field theoretic approach adopted in this paper image charges and their effects are naturally and systematically included by taking into account the fluctuations of the electrostatic field.

In section II we describe the field theory model we use to study the effects of non-linear terms on the surface charging

mechanism whilst retaining the free field theory description for the bulk electrostatic fields. This corresponds to using linear Debye theory in the bulk with fugacity μ but with the fully interacting description of the sources for the charging mechanism of the surfaces. The model is applied to a triple layer thin film as an idealized model of the surfaces where there is a Stern layer of thickness h from which all ions are excluded. In section III we discuss the mean-field solution to the field theory for the thin film for which the non-linear interactions at the surface determine the source terms in the mean-field equation. In section IV we give a detailed description of the effect of field fluctuations about the mean-field solution using the Schrödinger kernel approach developed in an earlier paper [23]. We give predictions for the surface charge $\sigma(L)$ and the disjoining pressure $P_d(L)$ as a function of film thickness L and show under reasonable assumptions that $\sigma(L) \rightarrow 0$ as $L \rightarrow 0$ and that the mean-field prediction for the large L tail of $P_d(L)$ is modified by one-loop corrections, both decaying like $\exp(-mL)$ for large L , where m is the Debye mass. In section V we present a number of example graphs and discuss their salient features. In particular, it is clear that the effects of image charges, which arise naturally and systematically in our formalism, are very strong and that qualitative predictions depend sensitively on the value of h , the thickness of the Stern layer. This demonstrates that a realistic model for the structure of the surface and the Stern layer in particular is necessary for a quantitative study. We also present some conclusions in this section.

II. MODEL

We consider an idealized model of a thin film made with nonionic soap adapted to the experimental set up used to measure the disjoining pressure as a function of the film thickness [3, 10, 17, 18, 19]. The film shown Fig. (1) consists of two parallel surfaces of area A the interior of which is filled with a monovalent electrolyte solution such as $NaCl$ in water with bulk dielectric constant ϵ . The exterior of the film is a dielectric medium of dielectric constant ϵ_0 , for example, air. The perpendicular distance between the two surfaces is denoted by $L + 2h$. The region of thickness h is the Stern layer from which the largest ions in the system are excluded and h can be taken to be the radius of the largest ion type in the system, which is here chosen to be the anion (in most physical systems it is the cation with the largest radius due to hydration). If the radius of the cation in solution is h' and $h' < h$ then the cation is excluded from a region of width h' from the surface but can be present in the region $[-(h - h'), 0]$ where there are no anions, thus leading to an effective surface charge in that region. Strictly speaking, just outside the film is the surfactant layer which in general will have a different dielectric constant to that of the exterior and the aqueous interior. Here for simplicity the presence of the nonionic surfactant is neglected. A version of this model with a single surface plus bulk is commonly used to model the surface properties of electrolyte solutions [15, 20, 21, 22]. In experiments the thickness L of the film may be varied by applying an external pressure in the cell containing the film and its bulk.

The grand partition function for this model system may be expressed as a functional integral

$$\Xi = \int d[\phi] \exp(S[\phi]) \quad (1)$$

where

$$S[\phi] = -\frac{1}{2} \int_{(T+L+2h) \times A} \beta \epsilon(\mathbf{x}) (\nabla \phi)^2 d\mathbf{x} + 2\mu \int_{L \times A} \cos(\beta e \phi) d\mathbf{x} \\ + \mu_+^* \int_{L \times A} (\delta(z) + \delta(L - z)) \exp(i\beta e \phi) d\mathbf{x}, \quad (2)$$

where e is the electron charge, A is the area of the film and $\beta = 1/k_B T$. The fugacities of the anions and cations are taken to be equal and denoted by μ as are their densities denoted by ρ . The total length in the z direction perpendicular to the film surfaces is $T + L + 2h$ where T denotes the total length external to the film. In the region $z \in [-h, L + h]$ the dielectric constant, which is a function only of z , is given by $\epsilon(z) = \epsilon$ and outside the film $\epsilon(z) = \epsilon_0$.

The above field theoretical formulation can be obtained directly from Quantum Electrodynamics [23] by retaining just the electrostatic potential field in the QED Lagrangian and coupling it to the distribution of ion charges. Alternatively, it can be obtained by standard field theory techniques based on the Hubbard-Stratonovich transformation for a monovalent Coulomb gas. The formulation takes into account both the Coulomb interactions between the ions and the zero frequency van der Waals forces due to fluctuations in the electrostatic potential [23]. These zero frequency van der Waals forces are particularly relevant when there are variations in the dielectric constants of the system since they naturally and systematically include the effects of image charges. This is especially the case for aqueous soap films in air where $\epsilon/\epsilon_0 \approx 80$. The density operators for the cations and anions can be shown to be

$$\rho_{\pm}(\mathbf{x}) = \mu \exp(\pm i e \beta \phi(\mathbf{x})) \quad (3)$$

The last term in Eq. (2) represents a highly localized affinity for the cations to be at the surfaces $z = 0$ and $z = L$ of the film, and is responsible for the generation of a surface charge. There are various mechanisms leading to affinities for ionic species at interfaces, ranging from chemical affinity to steric and entropic effects. Here this term arises in the following approximation. Since there can be cations in the region $[-(h - h'), 0]$ and the corresponding region $[L, L + (h - h')]$ there is, in addition to the first two terms of the action Eq. (2), a surface term

$$\Sigma = \mu \int_{[-(h-h'), 0] \times A} \exp(i\beta e\phi) d\mathbf{x} + \mu \int_{[L, L+(h-h')] \times A} \exp(i\beta e\phi) d\mathbf{x} . \quad (4)$$

This is the integral of the density operator given by Eq. (3) for the cations over the regions $[-(h - h'), 0]$ and $[L, L + (h - h')]$. These are the regions in the Stern layers which may be occupied by the cations but from which the anions are excluded. If $h - h' \ll l_D$, where l_D is the Debye length which characterizes the scale of the electrostatic interactions, then we can approximate Σ by

$$\Sigma = \mu(h - h') \int_{L \times A} \delta(z) \exp(i\beta e\phi) d\mathbf{x} + \mu(h - h') \int_{L \times A} \delta(z - L) \exp(i\beta e\phi) d\mathbf{x} \quad (5)$$

Comparing with the formula Eq. (2) we see that $\mu_+^* = \mu(h - h')$. In general actions of the type Eq. (2) can be used to describe various surface charging mechanisms with the proviso that the region where the surface charge is localized has a width much smaller than the Debye length, l_D . Whilst this description acts as a motivation for the model it is clear that in general there will in general be specific adsorption for the different species near the air water interface. To model a specific adsorption for the cations in the surface region $[-(h - h'), 0]$ we take a surface cation fugacity μ_s in this region which is greater than the bulk cation fugacity μ . On shrinking the surface region to zero one would then have $\mu_+^* = \mu_s(h - h')$. There is some evidence for specific absorption of certain ionic species at seemingly chemically neutral interfaces; the famous and controversial Jones-Ray dip [24] in the surface tension of weak electrolyte solutions (with interfaces with air) can be explained by invoking a specific adsorption of anions at the interface [25], although the basic surface exclusion model introduced in [20] and used here cannot explain negative excess surface tensions. Recent experimental evidence points towards a specific adsorption of hydroxide ions at air/water and oil/water interfaces [22]. In what follows we treat μ_+^* as an independent variable to account for the more complex charging mechanisms which can occur at the interface.

It is important to note that the fugacities μ and μ^* are determined by the values of the physical bulk density ρ and surface density for a single planar surface ρ_+^* . We then have

$$\rho = \mu \langle \cos \beta e\phi \rangle , \quad \rho_+^* = \mu_+^* \langle \exp(i\beta e\phi) \rangle ,$$

where the brackets stand for averaging over the bulk partition function. In mean-field theory this implies $\rho = \mu$, $\rho_+^* = \mu_+^*$ but this is not true in general and the relationship must be calculated taking field interactions into account.

In [23] the field theory with the action of Eq. (2) was analyzed in the weak-coupling or Debye-Hückel limit which is a Gaussian approximation where the action is expanded to second order in the field ϕ . This amounts to the assumption that the mean-field densities of cations and anions throughout the film are small enough so that $8\pi\rho(z)l_B^3 < 1$, where l_B is the Bjerrum length $l_B = e^2/\beta 4\pi\epsilon$. Another approach is to solve the full non-linear mean-field equations and then calculate the one loop correction which gives the effect of field fluctuations about this mean-field solution [27, 28]. In [27] the resulting mean-field solution in the case of fixed surface charge was ingeniously expressed in terms of special functions which allowed an analytic calculation of the one loop correction. In our case, however, the fact that the surface charge must be computed self consistently leads to additional complications and we take a different approach. We assume that the Gaussian approximation is valid inside the film but not at the surface where, because of the increased charge density, the electrostatic interactions will be stronger and we retain the full non-linear surface operators. The resulting theory can be analyzed as before [23] but with an effective L -dependent surface source for the field. The theory is accurate to the same order in perturbation theory as before but, in addition, now includes non-perturbative surface effects. The corresponding Debye-Hückel action with non-linear surface terms is

$$\begin{aligned} S^*[\phi] = & -\frac{1}{2} \int_{(T+L+2h) \times A} \beta\epsilon(z)(\nabla\phi)^2 d\mathbf{x} - \frac{1}{2} \int_{L \times A} \beta\epsilon m^2 \phi^2 d\mathbf{x} \\ & + \mu_+^* \int_{L \times A} (\delta(z) + \delta(L - z)) \exp(i\beta e\phi) d\mathbf{x} + 2\mu AL , \end{aligned} \quad (6)$$

where $m = \sqrt{8\pi\rho l_B} \equiv 1/l_D$ is the bulk Debye mass, l_D is the Debye length and l_B is the Bjerrum length defined above. The weak coupling limit corresponds to $m l_B < 1$, and the Gaussian approximation will be valid throughout

the film so long as the local or effective mean-field Debye mass $m(z) = \sqrt{8\pi\rho(z)} l_B$ does not become so large that this weak coupling condition is violated. This condition is $8\pi\rho(z)l_B^3 < 1$ as stated earlier. We note that since $\rho(z) > \rho_{bulk}$ this necessarily requires that $8\pi\rho_{bulk} l_B^3 < 1$.

Proceeding with the approximation scheme described above we have the expression

$$\Xi \approx \int d[\phi] \exp(S^*[\phi]) \quad (7)$$

for the grand partition function. The mean-field Poisson-Boltzmann equation is obtained from the saddle point of the action S^* :

$$\frac{\delta}{\delta\phi(\mathbf{x})} S^*|_{\phi_c} = 0 \quad (8)$$

with μ_+^* replaced by ρ_+^* . This is the correct procedure since perturbative corrections due to the interactions of field fluctuations about this mean-field, or tree level, solution will then relate ρ_+^* and μ_+^* self-consistently order by order. In principle, the same approach applies to the bulk quantities ρ and μ but since we are limiting the current analysis to a Gaussian theory in the bulk, the distinction need not be made at this stage.

Taking into account the Gaussian fluctuations about the mean-field solution gives the perturbative correction to one-loop for which we have

$$\Xi \approx \exp(S^*[\phi_c]) \int d[\phi'] \exp\left(\frac{1}{2} \int d\mathbf{x} d\mathbf{y} \frac{\delta^2 S^*}{\delta\phi(\mathbf{x})\delta\phi(\mathbf{y})}|_{\phi_c} \phi'(\mathbf{x})\phi'(\mathbf{y})\right), \quad (9)$$

with, again, μ_+^* replaced by ρ_+^* . All other terms are treated as interactions to be analyzed by perturbation theory.

The grand-potential per unit area of film J can be separated into a mean-field contribution plus the zero frequency van der Waals contribution coming from the fluctuations. We write

$$J = J^{MF} + J^{vdW} \quad (10)$$

where

$$J^{MF} = -\frac{1}{A\beta} S[\phi_c] \quad (11)$$

and

$$J^{vdW} = \frac{1}{2A\beta} \text{Tr} \ln \left(-\frac{\delta^2 S^*}{\delta\phi(\mathbf{x})\delta\phi(\mathbf{y})}|_{\phi_c} \right) \quad (12)$$

III. MEAN-FIELD THEORY

The mean-field equation is obtained as usual by looking for an imaginary solution to Eq. (8) $\phi_c = i\psi$ where ψ is real and corresponds to the mean-field electrostatic potential [23]. The resulting equation for ψ is

$$\beta\nabla \cdot \epsilon\nabla\psi - m^2\beta\epsilon\psi + \rho_+^*\beta e(\delta(z) + \delta(L-z)) \exp(-\beta e\psi) = 0, \quad (13)$$

within the film and outside the film one has

$$\beta\nabla \cdot \epsilon_0\nabla\psi = 0. \quad (14)$$

This mean-field equation has the form of a standard linearized Poisson-Boltzmann equation but with non-linear boundary terms with μ_+^* is replaced by its mean-field approximation ρ_+^* as explained in the previous section.

The solution for ψ is by symmetry only dependent on z and symmetric about the mid-plane of the film at $z = L/2$ and so we choose the solution $\psi(z) = C(L)\cosh(m(z - \frac{L}{2}))$ inside the film. Outside the film Eq. (14) gives that $d\psi/dz = 0$, which is the condition of electro-neutrality of the mean-field solution within the film. Integrating the mean-field equation between $z = 0^-$ and $z = 0^+$, and using the condition of electro-neutrality, one finds

$$\epsilon \frac{d\psi}{dz}|_{z=0^+} = -e\rho_+^* \exp(-\beta e\psi(0)) \quad (15)$$

Defining $D(L) = C(L) \beta e \cosh(mL/2)$ gives the non-linear self consistent equation determining D to be

$$D(L) = \alpha \coth\left(\frac{mL}{2}\right) \exp(-D(L)) \quad (16)$$

where $\alpha = m\rho_+^*/2\rho$ is dimensionless. In the Stern layer model $\alpha = m(h-h')/2 = (h-h')/2l_D$. As stated in Section II it is when $l_D \gg (h-h')$ that the formulation in terms of a surface charge is valid. In the study of this particular model one has that $\alpha \ll 1$, which also implies small surface charges compatible with the use of the quadratic approximation within the film. Then Eq. (16) may be formally solved as a power series in $\alpha \coth(\frac{mL}{2})$ using standard series inversion techniques from complex analysis. We find that

$$D(L) = \alpha \coth\left(\frac{mL}{2}\right) \sum_{n=0}^{\infty} (-1)^n \left(\alpha \coth\left(\frac{mL}{2}\right) \right)^n \frac{(n+1)^{n-1}}{n!} \quad (17)$$

We note that in general surface charge regulated models [7], even if there is an exact solution to the Poisson-Boltzmann equation (or its linearized form) in the bulk, one must determine the surface potential via a transcendental equation relating the surface charge to the surface potential which in general may be solved numerically by iteration [4] or by linearizing the boundary equation [5]. Fortunately in the case studied here we have an explicit series solution to the boundary equation. The disjoining pressure of a film $P_d(L)$ is the difference between the film and bulk pressures. In the grand canonical ensemble

$$P_d(L) = P(L) - P_{\text{bulk}} = -\frac{\partial J(L)}{\partial L} + \lim_{L \rightarrow \infty} J(L)/L \quad (18)$$

where J is the film grand potential per unit area. We can decompose the disjoining pressure into a contribution coming from the mean-field solution and a contribution coming from the field fluctuations which corresponds to the zero frequency van der Waals interaction

$$P_d^{MF}(L) = -\frac{\partial J^{MF}(L)}{\partial L} + \lim_{L \rightarrow \infty} J^{MF}(L)/L \quad (19)$$

$$P_d^{vdW}(L) = -\frac{\partial J^{vdW}(L)}{\partial L} + \lim_{L \rightarrow \infty} J^{vdW}(L)/L \quad (20)$$

After some straightforward but laborious algebra one finds that

$$P_d^{MF}(L) = \rho k_B T \frac{D^2(L)}{\cosh^2\left(\frac{mL}{2}\right)} \quad (21)$$

The mean-field value of the density within the film is given by

$$\rho_{MF}(\mathbf{x}) = 2\rho \cosh(e\beta\psi(\mathbf{x})) , \quad (22)$$

and in the linearized theory within the film this becomes

$$\rho_{MF}(\mathbf{x}) = 2\rho + \rho e^2 \beta^2 \psi(\mathbf{x})^2 . \quad (23)$$

At the mid-plane $z = L/2$ of the film one has

$$\rho_{MF}(z = \frac{L}{2}) - \rho_{\text{bulk}} = \rho \frac{D^2(L)}{\cosh^2\left(\frac{mL}{2}\right)} . \quad (24)$$

The mid-plane pressure formula [1, 2] for Poisson-Boltzmann theories with fixed surface charges or potentials, relates the disjoining pressure to the mid-plane mean-field density by

$$P_d^{MF} = k_B T [\rho_{MF}(z = \frac{L}{2}) - \rho_{\text{bulk}}] . \quad (25)$$

In fact, in theories of the type considered here with potentials at or near the film surface, one can show quite generally that the mid-plane formula holds generically as long as the external potential is zero in a finite interval containing

the mid-plane $z = L/2$. One can see directly, comparing Eq. (21) and Eq. (25) with the linearized approximation Eq. (24), that the mid-plane formula is respected here.

It is useful for what follows to work with the running variable $\alpha'(L) = D(L) \tanh\left(\frac{mL}{2}\right)$. The mean-field surface charge $\sigma_{MF}(L)$ may be written in terms of $\alpha'(L)$

$$\sigma_{MF}(L) = \frac{2\rho e\alpha'(L)}{m} \quad (26)$$

From Eq. (17) we have

$$\alpha'(L) = \alpha \sum_{n=0}^{\infty} (-1)^n \left(\alpha \coth\left(\frac{mL}{2}\right) \right)^n \frac{(n+1)^{n-1}}{n!} \quad (27)$$

As $L \rightarrow \infty$, α' takes its bulk surface value $\alpha^* = \lim_{L \rightarrow \infty} \alpha'(L)$. As mentioned previously we are using a Gaussian field theory inside the film and so the mechanism generating the surface charge cannot be taken to be too strong, implying that $\alpha \ll 1$ which gives $\alpha^* \approx \alpha$. As L decreases $\alpha'(L)$ decreases. However, since the expansion in Eq. (27) is in $\alpha \coth(mL/2)$, the non-linear terms in this series must be taken into account when varying L . Indeed, for small L one can show that $\alpha'(L) \sim -mL \ln(L)/2$, which tends to zero as L tends to zero.

The mean-field disjoining pressure in terms of $\alpha'(L)$ is

$$P_{MF} = \rho k_B T \frac{\alpha'^2(L)}{\sinh^2\left(\frac{mL}{2}\right)}, \quad (28)$$

which, in terms of the mean-field surface charge reads

$$P_{MF} = \frac{\sigma_{MF}^2(L)}{2\epsilon \sinh^2\left(\frac{mL}{2}\right)}. \quad (29)$$

For the linearized Poisson-Boltzmann equation with constant surface charge σ_c one finds that [8, 26]

$$P_{MF} = \frac{\sigma_c^2}{2\epsilon \sinh^2\left(\frac{mL}{2}\right)}. \quad (30)$$

Hence, at the mean-field level, fitting the disjoining pressure at each value of L with an L dependent σ_c will reproduce the behavior of $\sigma_{MF}(L)$ in the current theory. This result is also true for full non-linear mean-field theory and is not dependent on the quadratic field approximation in the bulk used here.

IV. FLUCTUATION EFFECTS

Evaluating the fluctuations about our mean-field solution yields

$$\begin{aligned} \frac{1}{2} \int d\mathbf{x} d\mathbf{y} \frac{\delta^2 S_{DH}}{\delta\phi'(\mathbf{x})\delta\phi'(\mathbf{y})} |_{\phi_c} \phi'(\mathbf{x})\phi'(\mathbf{y}) = & -\frac{1}{2} \int_{(T+L) \times A} \beta\epsilon(z) (\nabla\phi')^2 d\mathbf{x} - \frac{1}{2} \int_{L \times A} \beta\epsilon m^2 \phi'^2 d\mathbf{x} \\ & - \frac{1}{2} \beta\epsilon m \alpha'(L) \int_{L \times A} (\delta(z) + \delta(L-z)) \phi'^2 d\mathbf{x}, \end{aligned} \quad (31)$$

where

$$\alpha'(L) = D(L) \tanh\left(\frac{mL}{2}\right) = \frac{m\rho +^* \exp(-\beta e\psi(0))}{2\rho}. \quad (32)$$

The main difference in Eq. (33) from the pure Gaussian theory of [23] is that the surface term $\alpha'(L)$ is now a function of the film thickness, whereas in the pure Gaussian theory it is a constant. The fluctuation term Eq. (31) may be evaluated using functional techniques [14, 27, 29, 30, 31] as it is a functional determinant, or by path integral techniques [23]. Using the results of [23] one finds that the terms depending explicitly on α' and L that will contribute to the disjoining pressure and the surface charge are

$$\begin{aligned} \beta J^{vdW}(L, \alpha') = & \beta J_{\text{bulk}}^{vdW} L + \frac{m^2}{2\pi} \int dk \, k \ln \left(B(km)k + \alpha'(L) + \sqrt{k^2 + 1} \right) \\ & + \frac{m^2}{4\pi} \int dk \, k \ln \left(1 - \left(\frac{B(km)k + \alpha'(L) - \sqrt{k^2 + 1}}{B(km)k + \alpha'(L) + \sqrt{k^2 + 1}} \right)^2 \exp(-2Lm\sqrt{k^2 + 1}) \right), \end{aligned} \quad (33)$$

where

$$B(p) = \frac{1 + \Delta \exp(-2ph)}{1 - \Delta \exp(-2ph)}, \quad (34)$$

with $\Delta = (\epsilon_0 - \epsilon)/(\epsilon_0 + \epsilon)$. The term $\beta J_{\text{bulk}}^{vdW}$ in Eq. (33) is the van der Waals contribution to the bulk grand potential per unit volume and is given by

$$\beta J_{\text{bulk}}^{vdW} = \frac{m^2}{4\pi} \int dk k \left(\sqrt{k^2 + 1} - k \right). \quad (35)$$

The mean-field contribution to the bulk grand-potential per unit volume is simply $\beta J_{\text{bulk}}^{MF} = -2\mu$ since the mean-field solution in the bulk is just $\psi = 0$; there are no surfaces to set up a mean-field potential. At this point we may not replace μ by ρ because we need to work to one-loop for consistency. The total bulk grand-potential per unit volume is thus given by

$$\begin{aligned} \beta J_{\text{bulk}} &= -2\mu + \frac{m^2}{4\pi} \int dk k \left(\sqrt{k^2 + 1} - k \right) \\ &= -2\mu - \frac{m^3}{12\pi} + \frac{1}{8\pi} \Lambda m^2 + O\left(\frac{m^4}{\Lambda}\right) \\ &= -2\mu - g \frac{2\rho}{3} \left(1 - \frac{3\Lambda}{2m} \right) \end{aligned} \quad (36)$$

where Λ is a momentum space cut-off corresponding to a short distance cut-off $a \sim 1/\Lambda$ and $g = m^3/8\pi\rho = ml_B$. We see that indeed the expansion is in the dimensionless coupling g as asserted in section II. The bulk density of electrolyte is given by

$$2\rho = -\mu \frac{\partial}{\partial \mu} \beta J_{\text{bulk}} = 2\mu + \frac{m^3}{8\pi} - \frac{1}{8\pi} \Lambda m^2,$$

which can be written as

$$\mu = Z \rho, \quad Z = 1 - \frac{g}{2} \left(1 + \frac{\Lambda}{m} \right).$$

From its definition in section II we then also have, to this order in g , that $\mu_+^* = Z \rho_+^*$.

Substituting this result into Eq. (37) gives the well-known Debye expression for the bulk pressure

$$\beta P_{\text{bulk}} = -\beta J_{\text{bulk}} = 2\rho - \frac{m^3}{24\pi}. \quad (37)$$

In the field theoretic formulation used here the surface charge (on one surface) per unit area, σ , is given by

$$\sigma = e\mu_+^* \langle \exp(i e \beta \phi(z=0)) \rangle, \quad (38)$$

which becomes, to the order of accuracy of the present treatment,

$$\sigma = e\mu_+^* \exp(-e\beta\psi(z=0)) \langle 1 + i e \beta \phi'(z=0) - \frac{1}{2} e^2 \beta^2 \phi'^2(z=0) \rangle, \quad (39)$$

where the average $\langle \cdot \rangle$ in the above equation is over the fluctuations ϕ' . As the one-loop action in ϕ' is quadratic, the average of the term linear in ϕ' in Eq. (39) is zero and we may then write

$$\sigma = \frac{2\mu e \alpha'(L)}{m} - \frac{e \alpha'(L)}{2} \frac{\partial \beta J_{\text{bulk}}^{vdW}}{\partial \alpha'(L)}|_{\alpha'=0} + O(\alpha'^2), \quad (40)$$

where we have used that $\alpha = m\rho_+^*/2\rho = m\mu_+^*/2\mu$ and where we have kept only the leading order behavior of the surface charge in α' . The next order terms can be calculated and are finite though one needs to eliminate certain artificial divergences [32]. The formula Eq. (40) gives a surface charge susceptibility with respect to the conjugate variable α' . We note that the first term in on the right hand-side of Eq. (40) is simply the mean-field contribution to the surface charge σ_{MF} .

To $O(\alpha')$ we obtain

$$\sigma(L) = \frac{2e\alpha'(L)}{m} \left(\mu - \frac{m^3}{8\pi} \int \frac{kdk}{D_+(k, m)} + \frac{m^3}{16\pi} \int kdk \frac{D_-(k, m)}{D_+(k, m) [D_+(k, m)^2 \exp(2Lm\sqrt{k^2+1}) + D_-(k, m)^2]} \right) + O(\alpha'^2), \quad (41)$$

where $D_{\pm}(k, m) = kB(km) \pm \sqrt{k^2+1}$. There is, however, a divergence in the first integral term in Eq. (41). This term corresponds to the van der Waals contribution to the charge of a bulk surface $\sigma_{\text{bulk}} = \lim_{L \rightarrow \infty} \sigma$. This divergence can be regularized by choosing the fugacity μ to give the desired bulk electrolyte density ρ correct at one loop order. We define

$$\Gamma = \int kdk \left(\frac{1}{kB(km) + \sqrt{k^2+1}} - \frac{1}{2k} \right), \quad (42)$$

and then

$$\sigma_{\text{bulk}} = \frac{2e\alpha^*}{m} \left(\mu - \frac{m^3}{8\pi} \Gamma - \frac{m^2 \Lambda}{16\pi} \right), \quad (43)$$

where Λ is the ultra-violet cut-off introduced in the bulk calculation above. Note that for weak charging $\alpha^* \sim \alpha$. Hence in terms of the physical variable ρ we obtain the divergence-free formula for σ_{bulk}

$$\sigma_{\text{bulk}} = \frac{2e\alpha^*}{m} \left(\rho - \frac{m^3}{16\pi} - \frac{m^3}{8\pi} \Gamma \right). \quad (44)$$

We remark here that in the case $\Delta \neq 0$, if the Stern layer thickness h is taken to zero then the term Γ in Eq. (44) diverges. It is clear however that one cannot have a surface charge exactly at the interface between two media of different dielectric constants due to the presence of arbitrarily close image charges. The divergence in h as $h \rightarrow 0$ in Eq. (44) is thus a physical divergence and any model using a surface charge must place this surface charge away from a discontinuity in the dielectric constant. When $\Delta = 0$ no such divergence is present and $B(km) = 1$ leading to the simple formula

$$\sigma_{\text{bulk}} = \left(1 - \frac{g}{6} \right) \sigma_{MF}(\infty). \quad (45)$$

We notice that from Eq. (37) that this equation may be written as

$$\sigma_{\text{bulk}} = \frac{\beta P_{\text{bulk}} e \alpha^*}{m}. \quad (46)$$

From Eq. (44) we see that effect of electrostatic interactions is to reduce the surface charge from the value it would have had without interactions. This is because the excess anions left in the bulk pull the cationic surface charge into the bulk. The case where $\Delta > 0$ (*i.e.* $\epsilon_0 > \epsilon$) leads to $B(km) \geq 1$ for all k and, examining the integrand in the formula defining Γ , we find that $\Gamma < 0$ and hence that positive Δ increases the surface charge above that of the case $\Delta = 0$. This is to be expected physically as the image charges in this case attract the ions towards the medium of higher dielectric constant [16]. In the case where $hm \ll 1$ we may evaluate the integral defining Γ since the leading divergence as $hm \rightarrow 0$ comes from the large k integration. We find

$$\sigma_{\text{bulk}} = \left(1 - \frac{g}{6} + \frac{g\Delta}{4mh} \right) \sigma_{MF}(\infty). \quad (47)$$

Again, we see that for $\Delta > 0$ ($\Delta < 0$) the enhancement (reduction) of the surface charge which can be physically attributed to the presence of image charges.

Finally the L dependence of the surface charge at $O(\alpha')$ is given by

$$\sigma(L) = \sigma_{MF}(L) \left(1 - \frac{g}{2} - g\Gamma + \frac{g}{2} \int kdk \frac{D_-(k, m)}{D_+(k, m) [D_+(k, m)^2 \exp(2Lm\sqrt{k^2+1}) + D_-(k, m)^2]} \right), \quad (48)$$

where $D_{\pm}(k, m) = kB(km) \pm \sqrt{k^2+1}$.

Thus, because $\alpha'(L) \rightarrow 0$ as $L \rightarrow 0$, we find that σ_{MF} , and hence the surface charge σ , vanishes as the film becomes thin. This is a physical result which is not picked up by a pure Gaussian theory [23].

As previously stated the total disjoining pressure is composed of a mean-field contribution and a contribution coming from the fluctuations. We find the total of these two terms gives

$$P_d(L) = \frac{\sigma_{MF}^2(L)}{2\epsilon \sinh^2(\frac{mL}{2})} \left(1 + \frac{2(\sigma(L) - \sigma_{MF}(L))}{\sigma_{MF}(L)(1 + \alpha'(L) \coth(\frac{mL}{2}))} \right) - 4g \rho k_B T \int dk k \sqrt{k^2 + 1} \frac{f^2(k)}{1 - f^2(k)}, \quad (49)$$

where

$$f(k) = \frac{kB(km) + \alpha'(L) - \sqrt{k^2 + 1}}{kB(km) + \alpha'(L) + \sqrt{k^2 + 1}} \exp(-Lm\sqrt{k^2 + 1}). \quad (50)$$

In the derivation of this formula the divergences which arise at intermediate stages of the calculation can, as in the case of the surface charge, be shown to cancel in the final result.

The first term in Eq. (49) is simply the mean-field contribution to P_d , the second (in the same bracket) is the contribution coming from the dependence of J^{vdW} on L via the L dependence of α' . The last term is a form of screened zero frequency van der Waals contribution. In the absence of electrolyte we find that this last term gives a $1/L^3$ Casimir attraction across the film. In the presence of electrolyte this interaction is screened [14] and decays exponentially as $\exp(-2mL)$ which is twice as quickly as the mean-field contribution to the disjoining pressure which decays as $\exp(-mL)$ for large L . However in the theory presented here, the fluctuation effects give an additional term which decays also as $\exp(-mL)$ and hence the fluctuations modify the long distance behavior of P_d . We note theories with fixed surface charge the long-range component of the disjoining pressure is not altered at two-loop level and this effect is specific to charge regularized models. The strength and sign of this long range modification of P_d is controlled the ratio $(\sigma(L) - \sigma_{MF}(L))/\sigma_{MF}(L)$ which measures the relative deviation of the surface charge from its mean-field value. If the fluctuation effects enhance (reduce) the surface charge then the long range value of P_d is increased (decreased) from its mean-field value. The Casimir term is, however, is always attractive.

It should be remarked at this stage that to this order, $O(g)$, there will be L -dependent contributions from the non-Gaussian interaction term in ϕ'^4 . These contributions can be shown to vanish as $L \rightarrow \infty$ but their effect for finite L must be calculated. However, such a calculation requires the apparatus for the general perturbation theory to be developed which we shall present in a forthcoming paper [32].

V. DISCUSSION AND CONCLUSION

We have systematically developed a theory for a thin film with a full non-linear surface charging mechanism while retaining the free field theory description for the bulk electrostatic fields. This corresponds to using linear Debye theory in the bulk with fugacity μ but with the fully interacting description of the sources for the charging mechanism of the surfaces. We have applied the theory to a model consisting of a triple layer system, shown in Fig. (1), in which there is adsorption of cations on to the surface modelled by a surface fugacity μ_+^* and encoded in the dimensionless surface absorption strength parameter $\alpha = m\rho_+^*/2\rho$ where ρ and ρ_+^* are the bulk density and cation density on the surface of a bulk region, respectively, and m is the Debye mass. At the surface there is a Stern layer of thickness h from which all ions are excluded. The film is of thickness L and the dielectric constants are $\epsilon \sim 80\epsilon_0$ in the film and ϵ_0 outside the film. This model for a real surface is too simple but it encodes the important feature that the thermodynamic properties of the film are very strongly dependent on the detailed nature of the surface and its properties. This is due to two features: the charging mechanism which allows the surface charge to remain in equilibrium with the interior charges and the effect of image charges due to the discontinuity in the dielectric constant at the surface. First we determine the mean-field solution $\phi_c(z)$ using the non-linear surface operators as the source and then we use the Schrödinger kernel approach to calculate the partition function as an expansion in α and $g = ml_B$ where l_B is the Bjerrum length. Much of the details of this approach have been discussed in an earlier paper [23]. In this paper, we concentrate on the effects of the non-linear surface charging mechanism which leads us to introduce an effective, or running, surface charging parameter $\alpha'(L)$ and we analyze the behavior of the surface charge $\sigma(L)$ and the disjoining pressure $P_d(L)$ on m, α and h . The formulas summarizing our findings are Eqs. (48) and (49). Examples of the solutions to these equations are shown in Figs. (4) to (12) and we now briefly discuss the salient features of these results.

In Figs. (2) and (3) we show $\alpha'(L)$ as a function of L for various values of α and m , respectively. $\alpha'(L)$ controls the strength of the surface charging mechanism and from Eq. (16), and what follows, it is clear that $\alpha'(L) \rightarrow 0$ as $L \rightarrow 0$ which in turn causes σ_{MF} and σ to vanish also in this limit.

In Figs. (4) to (6) we show the dependence of P_d on h, m, α , respectively. From all these figures we see that the characteristic collapse transition is evident but that its strength is very sensitive to the parameters. In particular, from Fig. (4) we see that P_d decreases as h decreases, as we should expect since the image charges at the surface are repelling the cations and so reducing the surface charge. This effect can be seen directly in Fig.(9). The effect on P_d is due to the σ dependent term in Eq. (49) which arises because of the implicit L dependence of the free energy through its dependence on $\alpha'(L)$. Note that $\sigma_{MF}(L)$ is independent of h as in this formulation the effect of image charges first comes in at the one-loop level. The dependence of P_d on m and α shown in Figs. (5) and (6) has the expected trends but again the height of the peak in $P_d(L)$ is strongly dependent on the parameters which have been chosen to take values that can typically be achieved in experiment. In Fig. (7) we show the mean-field component and one-loop contributions for typical parameter values.

In Figs. (9) to (11) the behavior of the surface charge $\sigma(L)$ is shown. We see from Fig (9) that $\sigma(L)$ decreases very strongly with L for small L and that as h decreases the effect strengthens and that for sufficiently small h the value of $\sigma(L)$ has a zero and becomes negative. Ultimately, $\sigma(L) \rightarrow 0$ as $L \rightarrow 0$ and so must have a minimum value before turning towards the origin. These effects are due to the one-loop term in Eq. (48) and can be seen clearly in Fig. (12) where the mean-field and one-loop contributions to $\sigma(L)$ are separately shown. In Figs. (10) and (11) the trends shown are as expected but, as in the case of P_d the magnitude of $\sigma(L)$ is very sensitive to parameter values. The overall prediction is that $\sigma(L)$ is strongly dependent on L and vanishes as $L \rightarrow 0$.

In Fig. (8) we compare P_d for the linearized theory from ([23]) and the non-linear theory of this paper with $h = 0.3 \text{ nm}$. Although the peak in P_d occurs in much the same place it is lower in the non-linear theory for this value of h . Since the peak height is strongly dependent on h we see that a quantitative prediction requires a realistic model for the surface. See Fig. (9).

An important feature of these calculations is to note that the results are expressed as a series in both α or $\alpha'(L)$ and $g = ml_B$ with partial resummations in some cases. The major approximation is to use the free field theory within the bulk. The object was to study the effects of the non-linear surface charging mechanism and we have shown that these effects are indeed strong and it is clear that any approach which omits them or assumes a constant surface charge will be incorrect. Some of the effects are strong and there are features, such as the minimum in $\sigma(L)$ and its change of sign, that must be studied further in the full non-linear theory to see if they are not artifacts of the approximation. A consistent control over spurious and artificial infinities must await the full perturbation theory. An example is eluded to in Eq. (40) and what follows. We have indicated how to control such quantities here to the one-loop level and see that even here the analysis is rather delicate. There are, in principle, $O(g)$ terms from interactions within the bulk which will vanish as $L \rightarrow \infty$ but contribute finite L effects to P_d and σ but these terms are not expected to be large. We shall present an analysis of all these topics in a forthcoming paper [32] in which the full non-linear theory and its perturbation expansion will be studied.

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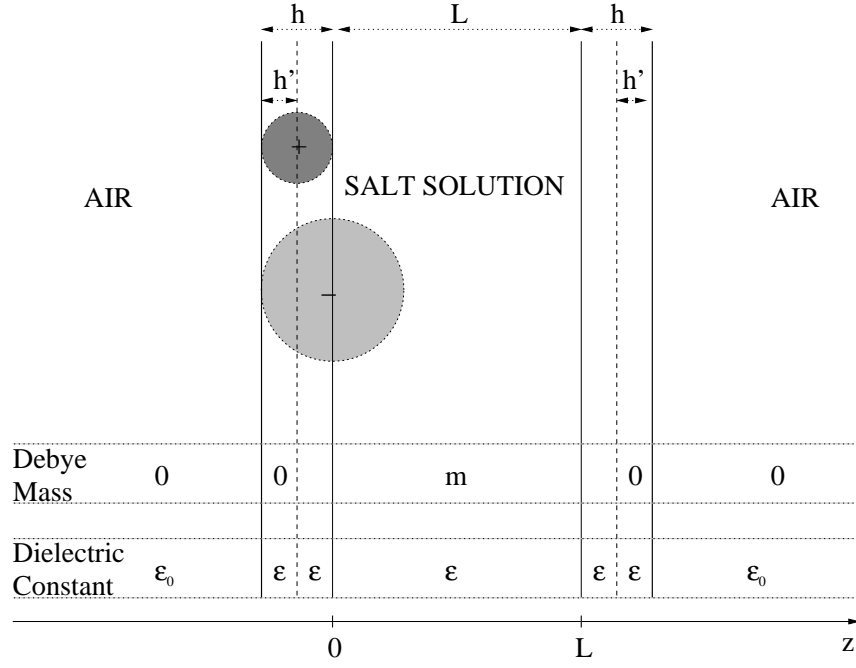


FIG. 1: Cross section through a model soap film. The distance of closest approach of the ions to the surfaces (at $z = 0$ and $z = L$) is the effective radius of the ionic species in solution. The dielectric constants and Debye masses as a function of the distance perpendicular to the film surface (*i.e.*) as a function of the position on the z axis are also shown.

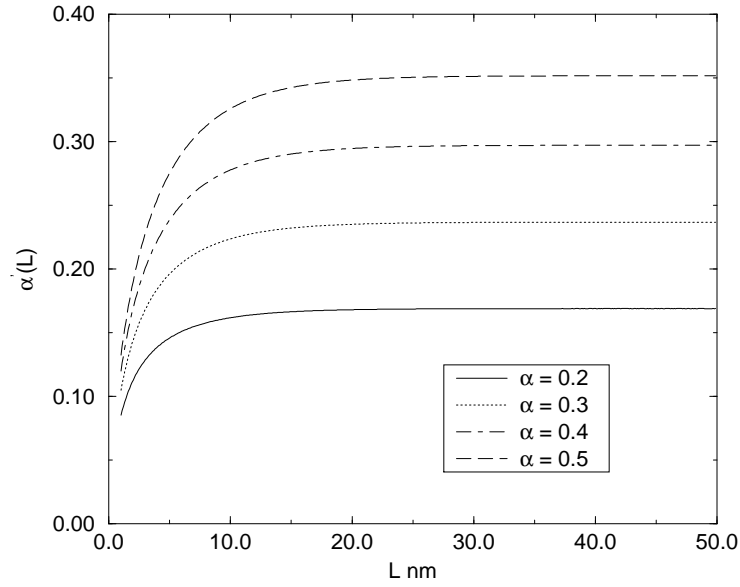


FIG. 2: $\alpha'(L)$ for Debye mass $m = 0.2 \text{ nm}^{-1}$ and $h = 0.3 \text{ nm}$ for values of $\alpha = 0.2, 0.3, 0.4, 0.5$ which controls the strength of the surface charging adsorption.

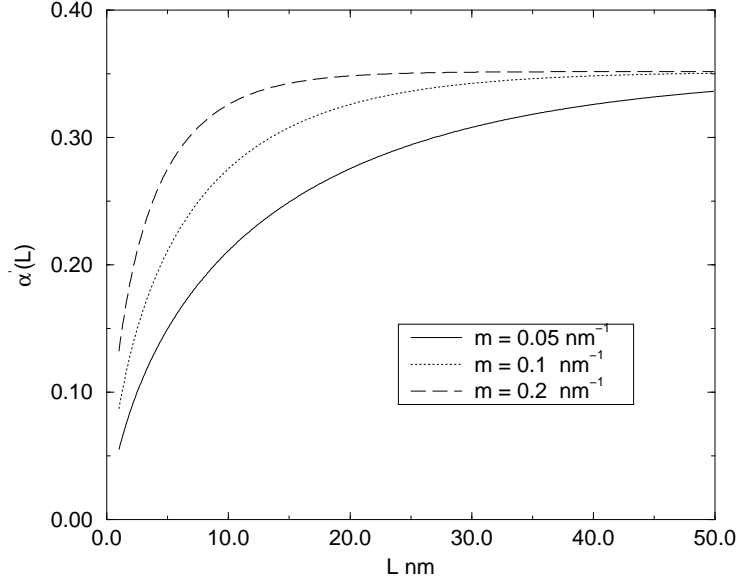


FIG. 3: $\alpha'(L)$ for $\alpha = 0.5$ and Stern layer thickness $h = 0.3$ nm for values of Debye mass $m = 0.05, 0.1, 0.2$ nm $^{-1}$.

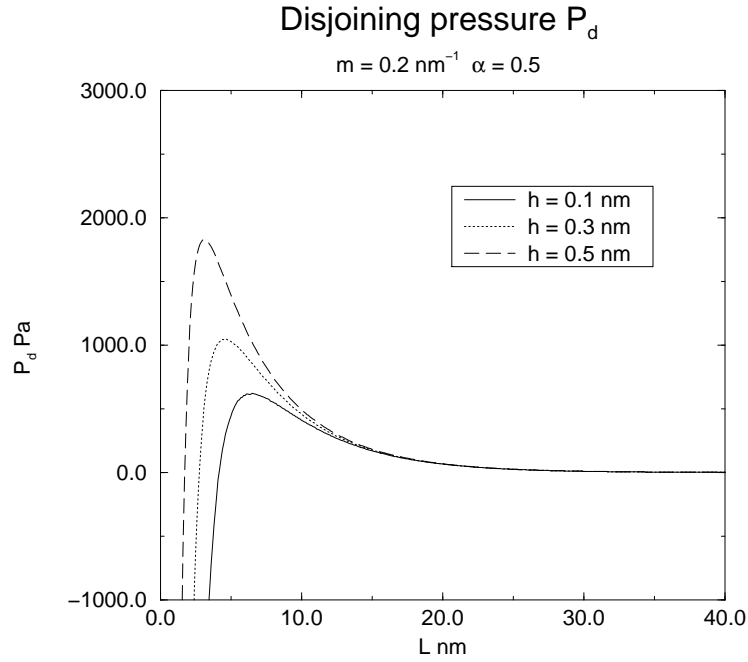


FIG. 4: The disjoining pressure given in Eq. (49) for Debye mass $m = 0.2$ nm $^{-1}$ and $\alpha = 0.5$ for different values of the thickness of the Stern layer $h = 0.1, 0.3, 0.5$ nm. The sensitive dependence of P_d on h is evident as we should expect since the influence of the image charges increases rapidly as h decreases.

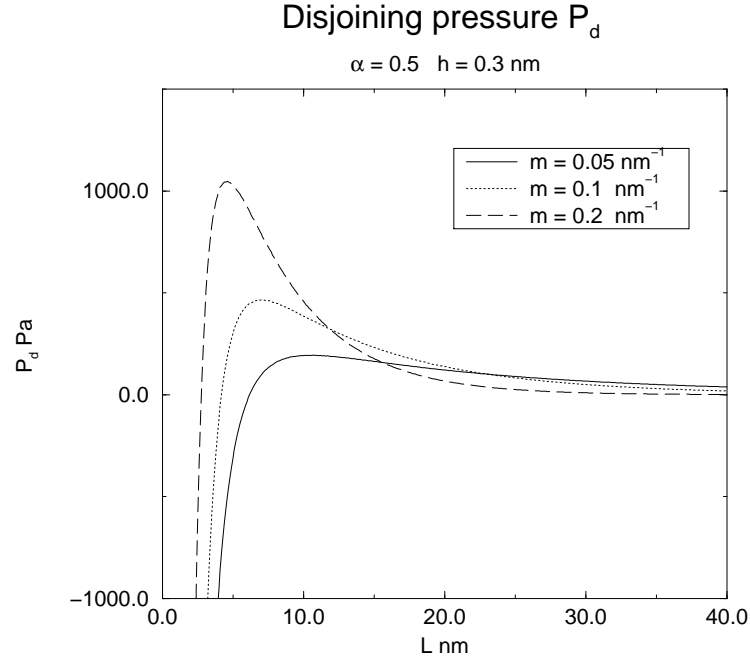


FIG. 5: The disjoining pressure given in Eq. (49) for $\alpha = 0.5$ and Stern layer thickness $h = 0.3$ nm for values of the Debye mass $m = 0.05, 0.1, 0.2$ nm⁻¹.

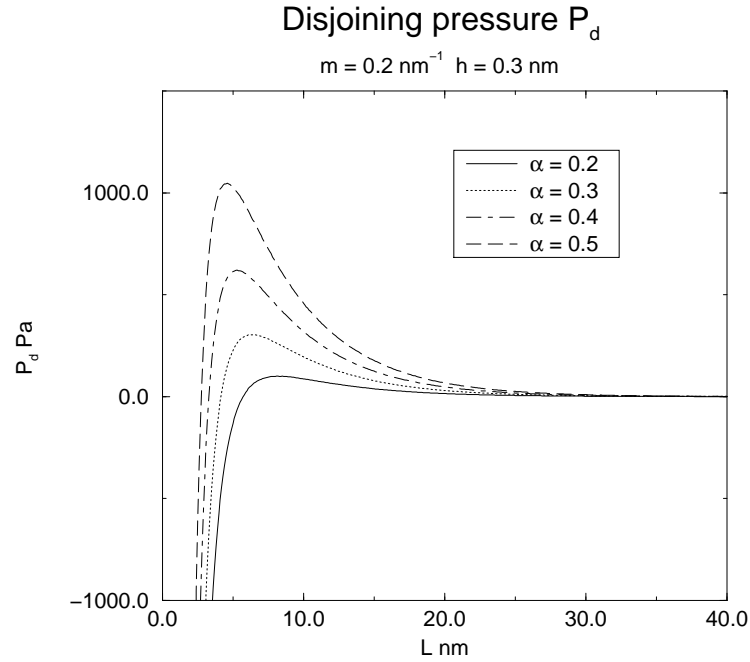


FIG. 6: The disjoining pressure given in Eq. (49) for Debye mass $m = 0.2$ nm⁻¹ and Stern layer thickness $h = 0.3$ nm for values of $\alpha = 0.2, 0.3, 0.4, 0.5$.

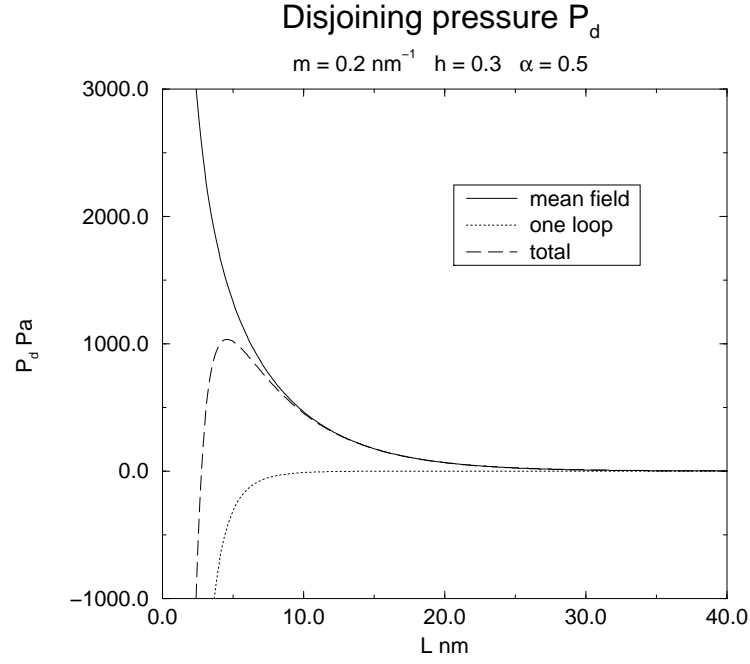


FIG. 7: The disjoining pressure given in Eq. (49) showing the mean-field contribution and the one-loop ($O(g)$) contributions as a function of Stern layer thickness $h = 0.3$.

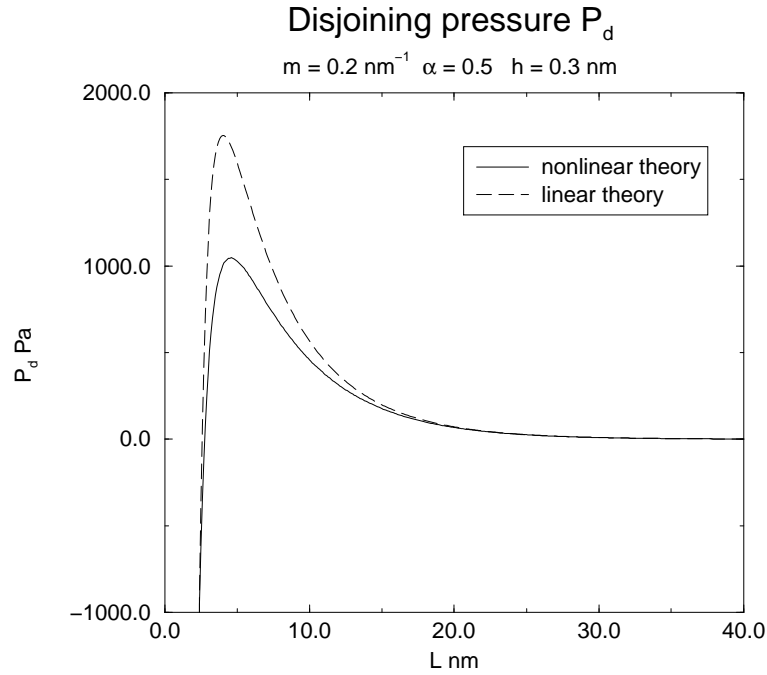


FIG. 8: The disjoining pressure given in Eq. (49) for $m = 0.2 \text{ nm}^{-1}$ and $\alpha = 0.5$ for the linearized theory from ([23]) and the non-linear theory of this paper for which $h = 0.3 \text{ nm}$. Although the peak in P_d occurs for much the same value of L it is lower in the non-linear theory for this value of h . Since the peak height is strongly dependent on h we see that a quantitative prediction requires a realistic model for the surface. See Fig. (9).

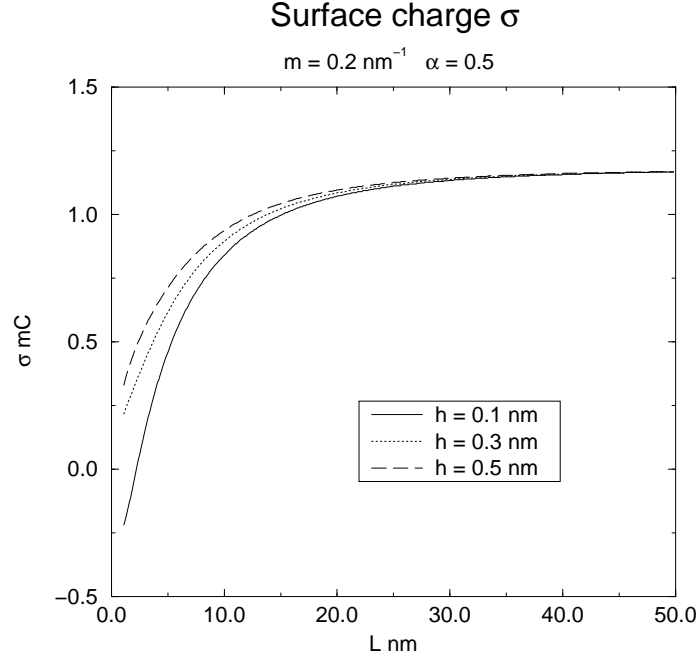


FIG. 9: The surface charge σ in millicoulombs in Eq. (48) for Debye mass $m = 0.2 \text{ nm}^{-1}$ and $\alpha = 0.5$ for different values of the thickness of the Stern layer $h = 0.1, 0.3, 0.5 \text{ nm}$. We see that σ decreases with L and this effect is enhanced as h becomes smaller as we should expect since the image charges have greater influence. However, even though σ is constrained to vanish we see that for small enough h it changes sign and so must have minimum at very small L before turning towards zero. This effect is evident in Fig (12). Whether or not this effect is an artifact will be a subject of further study.

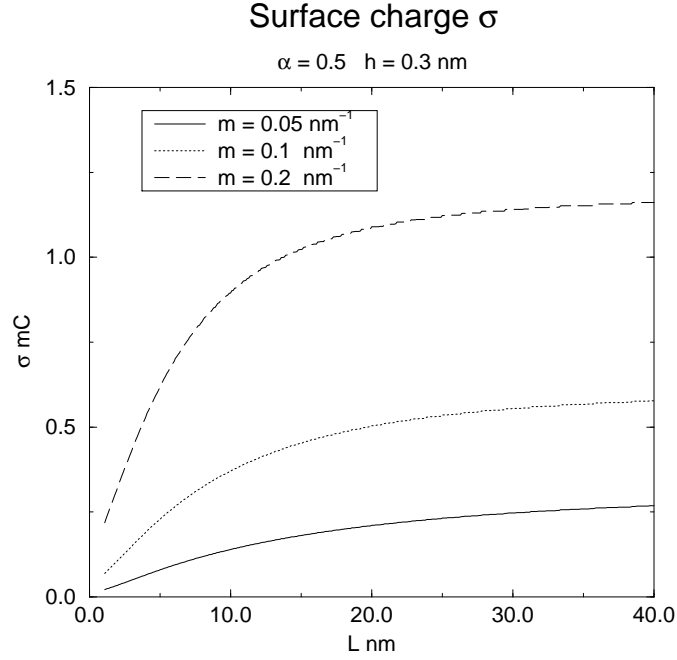


FIG. 10: The surface charge σ in millicoulombs in Eq. (48) for $\alpha = 0.5$ and Stern layer thickness $h = 0.3 \text{ nm}$ for values of the Debye mass $m = 0.05, 0.1, 0.2 \text{ nm}^{-1}$.

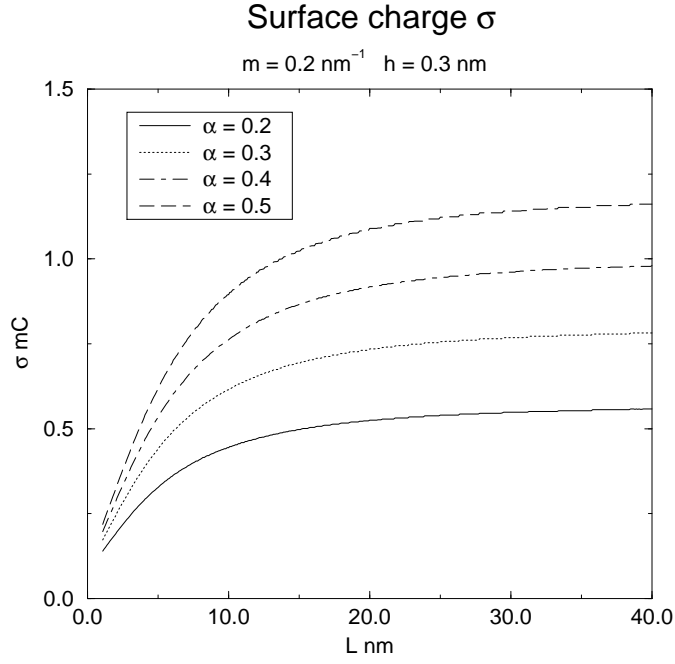


FIG. 11: The surface charge σ in millicoulombs in Eq. (48) for Debye mass $m = 0.2 \text{ nm}^{-1}$ and Stern layer thickness $h = 0.3 \text{ nm}$ for values of $\alpha = 0.2, 0.3, 0.4, 0.5$.

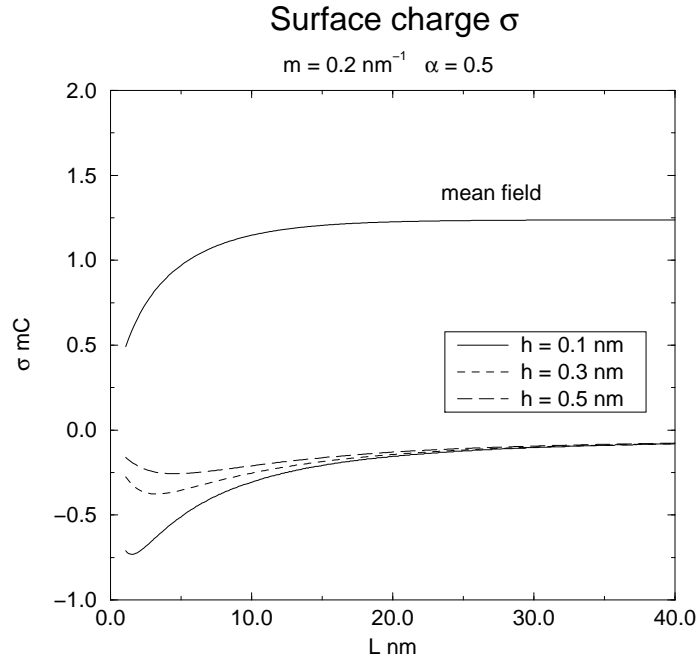


FIG. 12: The surface charge σ in millicoulombs in Eq. (48) showing the mean-field contribution and the one-loop ($O(g)$) contributions as a function of Stern layer thickness $h = 0.1, 0.3, 0.5 \text{ nm}$. The one-loop contribution is negative and has a minimum before turning to zero as it must since $\alpha'(L)$ vanishes as $L \rightarrow 0$.